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The Effect of Ta_2O_5 on the Interaction Between Silicon and Its Contact Metallization

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ABSTRACT

Evidence is presented showing that the presence of the commonly used anti-reflection coating material, Ta_2O_5, on the free surface of contact metallization can either suppress or enhance, depending on the system, the interaction that takes place at elevated temperatures between the metallization and the underlying silicon. The Ta_2O_5 layer is shown to suppress both the generation and the annihilation of vacancies at the metal free surface which are necessary to support metal-silicon interactions. Evidence is also presented indicating that the mechanical condition of the free metal surface has a significant effect on the passivating ability of the Ta_2O_5 layer.

Introduction

Properly sintered contacts are essential to ensure high output from a solar cell. Good adhesion and good electrical contact require that the metallization be thermally treated subsequent to deposition on the semiconductor surface. While the sintering conditions for ohmic rear contacts are not too critical, times and temperatures must be carefully chosen for the front contacts because of the proximity of the junction. Thermal treatment must in this case be thorough enough to ensure good electrical contact but not so severe as to cause degradation of the junction.

During an investigation of the causes of the low temperature power loss phenomenon known as the flat-spot effect, it was determined that sintering can cause localized dissolution of the silicon substrate into the contact metallization resulting in destruction of the junction in those regions.[1] The resulting geometry is described schematically in figure 1. As shown in the figure, we have found that a relatively low temperature (400-500°C) heat treatment can cause a localized reaction between the metal and the silicon substrate that results in the perforation of the emitter. In these regions metal-like contact is made directly to the cell base. The equivalent circuit for this configuration, shown in figure 2, insert, is that of a resistive metal-semiconductor-like interface in parallel with the original PN junction. The resultant I-V characteristics of such a combination (known as the flat-spot effect and observed most easily at low temperature) is a result of summing the normal PN characteristic with that of the MSL interface (figure 2).

When the metallization is removed from a cell that has been heat treated to induce flat-spot behavior, the underlying silicon is invariably observed to be pitted. In the case of the normally used TiPdAg contacting, the pits are regions where the silicon substrate has dissolved into the contact metallization. In this particular materials system the reaction proceeds rapidly when the temperature exceeds 450°C.

In the course of our studies of the Si-TiPdAg system it was observed that the application of the commonly used anti-reflection coating material, Ta_2O_5, over the free surface of the contact metallization could prevent the interaction which causes pitting in the underlying silicon. This effect is illustrated in figure 3 for a cell that was heated for 2 hours at 560°C in an inert atmosphere. Prior to the heat treatment, one-half of this cell was coated with 600 Å of Ta_2O_5. The figure shows the border region between the coated and the non-coated regions and, as can be seen, pitting is completely suppressed in the region overcoated with Ta_2O_5.

The purpose of this paper is to present the results of our investigations into the causes of the passivating effects of the Ta_2O_5 overcoating.

Basic Mechanism

As illustrated in figure 3, the Ta_2O_5 coating on the surface of the metallization apparently prevents the reaction that would normally take place between the silicon and the adjacent titanium metal. In order to understand the mechanisms operating here, it is helpful to look closely at the details of the titanium-silicon reaction. According to the literature this reaction is unilateral, i.e., silicon diffuses into the titanium with little or no diffusion of titanium into the silicon.[2] It has also been established that when two solids interdiffuse via a vacancy interchange mechanism, any imbalance in the diffusion rates is compensated for by a flow of vacancies in a direction opposite to that of the faster diffusing species.[3] In the present case, therefore, the unilateral flow of silicon atoms into the titanium lattice requires an equal and opposite flow of vacancies through the metal toward the

silicon. The large volume of vacancies needed to support the unilateral silicon diffusion must be generated either at a free surface or in a region of high lattice disorder. Indeed the most likely source in this case is the free surface o the contact metallization. Vacancies generated at this surface must then diffuse through the metal toward the silicon as required to support the diffusion of silicon into the metallization. It is suggested that the effect of the Ta_2O_5 overcoating on the metal surface is to disturb the vacancy generating ability of this surface and th s to affect the rate of silicon diffusion into the metal. The suppression of pitting by the Ta_2O_5 overcoating is, therefore, explained by its ability to retard vacancy formation at the free metal surface.

If the above reasoning is correct, the effect of the Ta_2O_5 overlayer should vary depending on the metallization system used. We should expect different behavior, for example, between systems in which silicon is the primary diffuser (Ti[2], Au[4], Fe[5], Al[4], Hf[6]), those in which the metal is the primary diffuser (Ni, Mg)[5], and those in which the metal and the substrate interdiffuse at roughly equal rates (Pt[7], Pd[5]).

Effects of Lattice Disorder

Before discussing other systems, it should be mentioned that there is one area where the Ta_2O_5 overcoating is not effective in suppressing pitting in the TiPdAg system, i.e., at the edges of the metallization. Figure 4 illustrates the failure of the Ta_2O_5 overcoating to suppress pitting at the metallization edges. Pitting is observed along the edges of the contact finger after heat treatment even though the cell was overcoated with Ta_2O_5. (Special care was taken here to ensure that all metal surfaces, both normal and perpendicular to the silicon surface were coated.) In contrast, the silicon surface under the rest of the metallization is undisturbed.

The cause of this behavior is believed to be the presence of localized lattice disorder along the edges of the metallization which permits vacancy generation in these regions in spite of the presence of a Ta_2O_5 layer. To illustrate the vacancy generating ability of a disordered metal surface, the following experiment was performed. After evaporating TiPdAg over the entire area of a 2 x 2 cm wafer, a vertical stripe, a few mm wide, was made across the wafer by gently abrading the Ag surface with a standard pencil eraser. The lower half of the wafer was then coated with Ta_2O_5 after which it was subjected to a 560°C, 2 hour heat treatment. Figure 5 shows the resulting silicon surface after metal removal. As can be seen, the silicon surface under the abraded and overcoated metal (lower center) has become just as pitted as the regions that had not been overcoated (upper). On the other hand, the overcoated regions that had not been abraded show no sign of pitting. Also, a close look (figure 6) reveals that the pits in the abraded region are arranged in linear arrays parallel to the scratch patterns that had been present on the metal surface. The conclusion is, therefore, that the damaged regions are apparently capable of supplying a vacancy flux sufficient to support silicon dissolution even though the metal surface had been overcoated with Ta_2O_5.

Having established that lattice disorder in the metallization can render the Ta_2O_5 overcoating ineffective, the next task is to show that the metallization edges are regions of lattice disorder. We can do this by considering the mechanical stresses generated in the cell contacts due to the differences in thermal expansion between the cell and the contacts. Zeyfang,[8] for example, has calculated the magnitude and distribution of the stresses developed in a thin plate of finite dimensions bonded to a semi-infinite substrate with a different thermal expansion coefficient. According to these calculations, the stresses induced in the plate as the temperature is varied are not uniformly distributed. They are, in fact, found to be concentrated almost entirely at the edges of the plate. Depending on the circumstances these stresses could exceed the yield point of the plate and the resulting plastic flow would result in a concentration of lattice disorder in these regions. It is suggested, therefore, that thermal excursions subsequent to the deposition of the contact metallization are, in general, sufficient to cause lattice disorder near the edges of the contact metallization. These regions would then act as vacancy sources and support localized dissolution of the underlying silicon even though a Ta_2O_5 overcoating may have been applied. It would follow that this type of pitting should be able to be prevented by eliminating large ($T > 300°C$) temperature excursions after metal deposition.

Effect of Various Metallization Systems

If the vacancy suppression mechanism is correct, we should expect, as mentioned previously, that the effectiveness of the Ta_2O_5 overlayer would vary according to the diffusion characteristics of the system. We would expect, for example, that the overlayer would be more effective in the case where silicon is the primary diffuser than when the opposite is true. To test this hypothesis, we studied the interaction of silicon with three classes of metals. The first group consisted of those metals which, like titanium, do not diffuse into silicon, i.e., Au, Fe, Hf, and Al. The second group, Pt and Pd, were those metals that interdiffuse at roughly equal rates with the silicon substrate. The third group consisted of Ni and Mg which diffuse unilaterally into silicon, i.e., with little or no silicon diffusion into the metal. The silicon substrates were 10 ohm-cm resistivity, p-type, with phosphorous diffused junctions. The initial sheet resistances were about 70 ohm/□. Both the metal layers and the Ta_2O_5 overcoatings were deposited via electron beam evaporation.

Before describing the results of these experiments, it is useful to consider in more detail the mechanisms operating in the TiPdAg system. The fact that we are able to observe the passivating effects of Ta_2O_5 on the silver free surface implies that the other interfaces, i.e., the TiPd and the PdAg interfaces, are not vacancy-producing regions. If either one of these interfaces were active vacancy sources, the effect of the Ta_2O_5 on the free surface would be masked to a greater or lesser extent by the flow of vacancies from these other sources. Thus, even though the Ta_2O_5 layer is active in suppressing vacancy generation, we may not be able to observe it because of the action of the other interfaces in the system.

Group I: In analogy to the TiPdAg system, the first attempts with these metals involved depositing a three component metal layer, i.e., 1000 Å of the metal to be studied, 1000 Å of Pd, and 3 um of Ag. Half of each sample was then coated with about 600 Å of Ta_2O_5 after which the wafers were heat treated at 570°C for 1 hour in an inert atmosphere. Examination of the resulting silicon surfaces indicated that in every case pitting had occurred uniformly across the samples. Since it was suspected that the pitting may have been caused by vacancies generated at one of the internal interfaces, another set of samples was prepared and processed, this time eliminating the Pd layer and the interfaces associated with it. The results in this case (table I) did show evidence of the reaction inhibiting effect of the Ta_2O_5 coating. Aluminum, which showed uniform pitting on both the coated and the noncoated regions, was the only metal that did not behave as expected.

While the AuAg sample showed a marked decrease in pitting on the coated side, the pitting that did occur there suggests that the Au-Ag interface may have some vacancy generating ability. While the FeAg and the HfAg samples showed no pitting whatsoever, sheet resistance measurements showed significantly lower values on the coated side indicating a suppression of the interaction there. The metal-silicon interaction in these two systems evidently proceeds more homogeously than in the titanium or the gold systems. The failure of the AlAg system to show less pitting on the coated side could possibly be due to significant vacancy generation at the AlAg interface. Also, the results may have been influenced by the proximity of the heat treatment temperature to the Al-Si eutectic point (577°C).

While the results for these systems are not as clear-cut as those in the TiPdAg system, they are all consistent with the vacancy suppression model.

Group II: For this run, 1000 Å of either Pt or Pd were deposited, followed by 3 um of Ag. Processing was the same as for Group I. As seen in the table, uniform pitting was observed in both cases, and while it is difficult, as mentioned above, to draw conclusions from negative results, the data are not inconsistent with the proposed mechanism.

Group III: 1000 Å of either Ni or Mg were deposited under a 3 um layer of Ag. The samples were then processed as before. Examination of the resulting silicon surfaces after processing showed that in this case the Ta_2O_5 actually enhances the metal-silicon interaction rate. Figure 6 shows the silicon surfaces of a cell that had been contacted with MgAg. The left half of the cell was coated with Ta_2O_5 prior to heat treatment. As can be seen, the wafer is more severly pitted where they had been overcoated with Ta_2O_5.

This behavior can be explained using the vacancy suppression model if one makes the assumption that a surface that is a poor source of vacancies also is a poor sink for vacancies. We will assume, in other words, that the Ta_2O_5 overcoating suppresses not only the generation but also the annihilation of vacancies at the free surface. If this is so then the large volume of vacancies that is being pumped into the metallization by the unilateral diffusion of metal atoms in the opposite direction will be reflected rather than absorbed at the overcoated free surface. This has the effect of raising the vacancy concentration in the sample, thus enhancing the metal-silicon reaction rate.

The data from these three sets of experiments thus appear to be consistent with the Ta_2O_5 vacancy suppression model.

Conclusions

The major conclusions to be drawn from the preceding analysis are:

1. Silicon-metal reactions in systems in which silicon is the primary diffuser can be suppressed by overcoating the as-deposited metal with Ta_2O_5. This has been demonstrated for the TiPdAg, AuAg, FeAg, and HfAg metallization systems.

2. The Ta_2O_5 overcoating has no effect in systems in which both silicon and the contacting metallization interdiffuse at equal rates. This has been shown for the PdAg and the PtAg systems.

3. Silicon-metal reactions in systems in which the metal atom is the primary diffuser can be enhanced by a Ta_2O_5 overcoating. This has been demonstrated for the NiAg and the MgAg metallization systems.

4. The Ta_2O_5 overcoating apparently prevents both the generation and the annihilation of vacancies at the free metal surface which are necessary to support the metal-silicon interaction.

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5. The Ta_2O_5 overcoating is not effective if the metal surface is highly disordered.

6. The edges of the cell metallization have been found to be sites of considerable lattice disorder due to differences in thermal expansion coefficient between the silicon substrate and the contacting metal.

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Table I - Silicon surface pitting after 1 hour, 570°C, inert atmosphere.

	With Ta_2O_5	Without Ta_2O_5
Group I		
AuAg	light pitting	heavy pitting
FeAg	none, R_s = 65 ohm/□	none, R_s = 85 ohm/□
HfAg	none, R_s = 85 ohm/□	none, R_s = 105 ohm/□
AlAg	uniform pitting	uniform pitting
Group II		
PtAg	uniform pitting	uniform pitting
PdAg	uniform pitting	uniform pitting
Group III		
NiAg	very heavy pitting	heavy pitting
MgAg	very heavy pitting	heavy pitting

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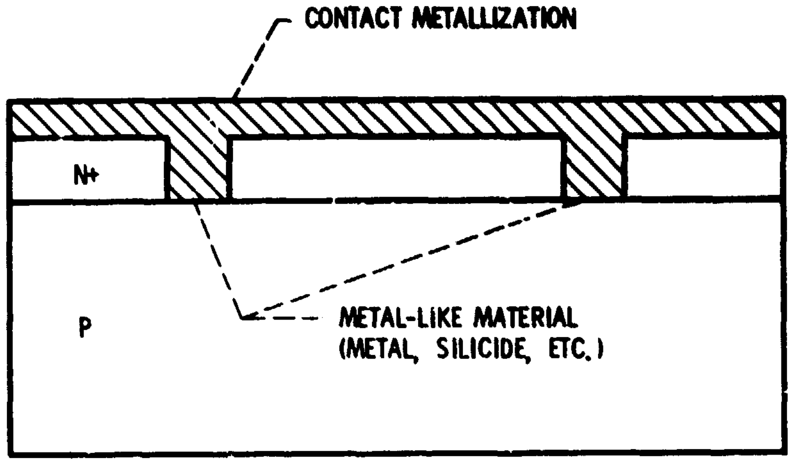


Figure 1. - Schematic cross section showing result of localized metal-silicon interdiffusion.

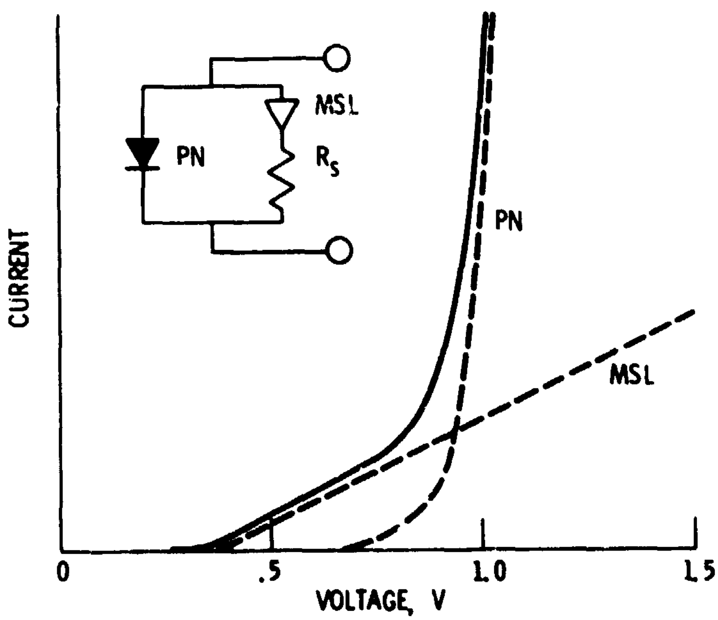
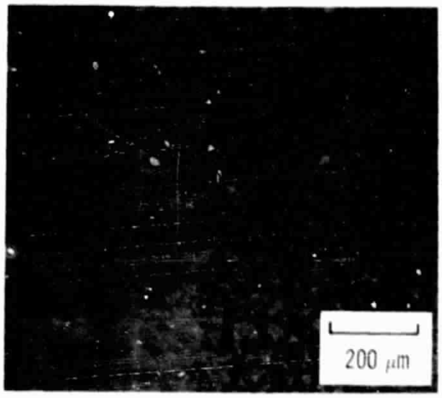


Figure 2. - Schematic diagram of FS mechanism. Solid curve is sum of PN and MSL characteristics.



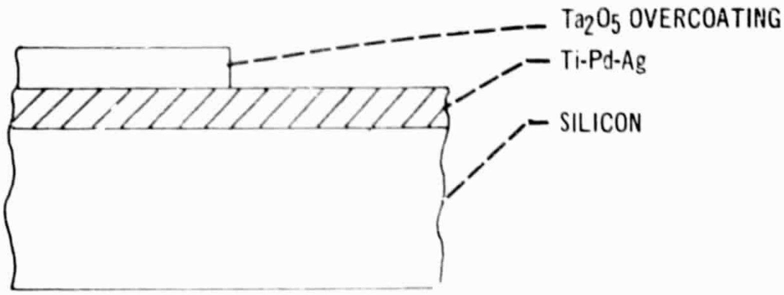


Figure 3. - Effect of Ta_2O_5 overcoating on silicon surface pitting heat treatment, 560 °C for 2 hr; inert atmosphere.

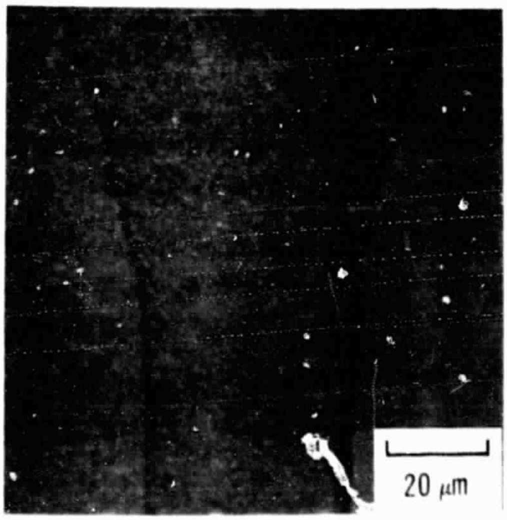


Figure 4. - Pitting observed at metallization edges after 2-hr. 560° C heat treatment with Ta_2O_5 overcoat applied.

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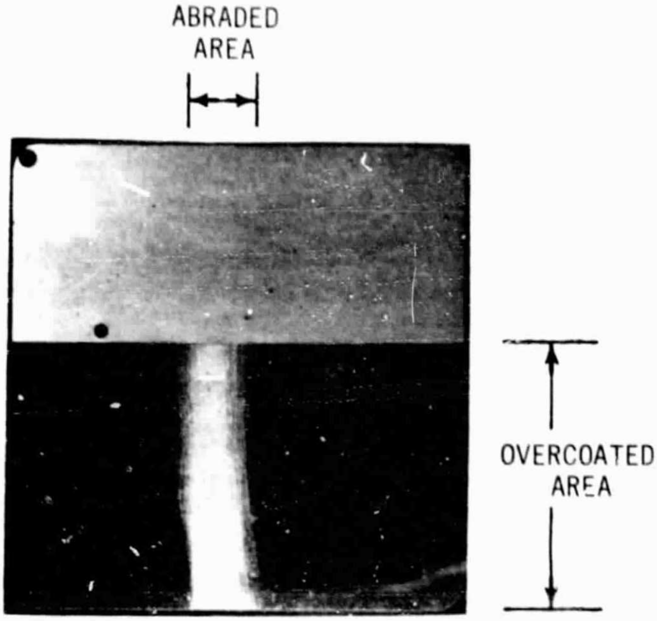

Figure 5. - Effect of surface abrasion on Ta_2O_5 passivation. Silicon surface, metallization removed.

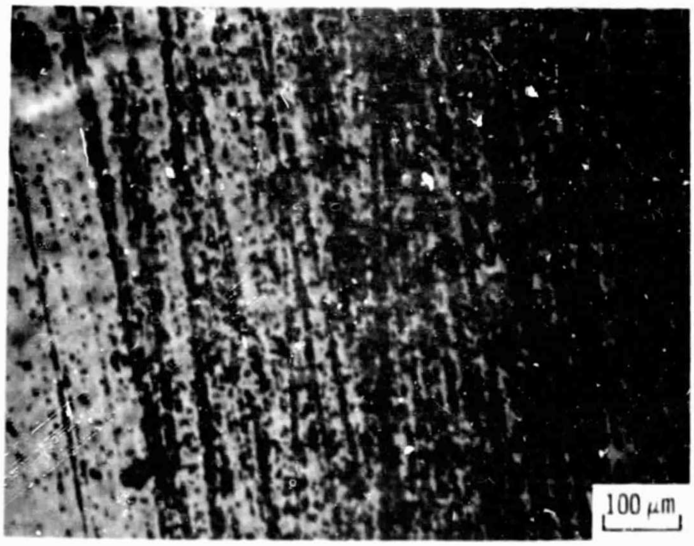

Figure 6. - Magnified view of silicon surface under abraded area of figure 5.

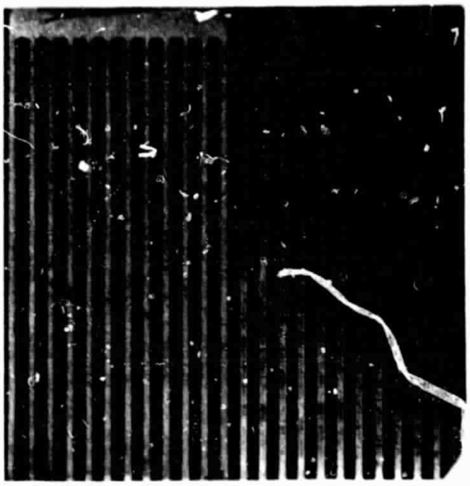

Figure 7. - Silicon surface of a M_gA_g contacted cell. Ta_2O_5 coating on left half caused severe pitting during heat treatment.